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ELONGATION HYSTERESIS OF HEVEA AND SYNTHETIC ELASTOMERS[1]

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Abstract

A hysteresis test has been developed which measures directly the energy loss per cycle of elongation. Six samples are stretched, like the spokes of a wheel, between a small disk and a large disk. The large disk is motor driven, and the small disk, mounted on a ball bearing, is displaced eccentrically with respect to the larger disk. In the elongation cycle which each sample undergoes with each revolution, the hysteresis causes an average force on the small disk which is normal to the eccentric displacement and is proportional to the energy loss per cycle. A lever and balance system makes it possible to measure this force continuously while the machine is running.

Measurements were made on gum stocks of Hevea and five commercial synthetic elastomers. Testing conditions included temperatures, T, of 0°, 35°, 70°, and 105°C., frequencies, f, of 5 and 50 c.p.s., mean elongations, e, of 50, 100, and 200%, and elongation amplitude, A, 25%. Absolute hysteresis, H, (loss/cycle-(amplitude)^2) at first decreases with increasing e and then flattens or goes through a minimum. Hysteresis decreases with increasing T. The temperature coefficient between 0° and 35°C. is very large for Hycar. Hysteresis usually increases with f, but only slightly in most cases; and Hevea at e = 400% shows a reversal of frequency effect, which is presumably associated with crystallization effects.

Under the same test conditions, the hysteresis of the synthetics is 10 to 20 times that of Hevea.

When the hysteresis data for all synthetic stocks at various temperatures are plotted against $T-T_s$, T_s being second order transition temperature of the respective elastomer, the data lie within a rather narrow band. From this it is concluded that the hysteresis of synthetic elastomers arises from the same molecular forces which cause hardening and embrittlement at and below T_s.

Introduction

In many of the service conditions in which rubber is subjected to repeated cycles of deformation, the operating frequencies lie in the range from 1 to 100 c.p.s. Most hysteresis testing at such frequencies has in the past been carried out with equipment which imposed narrow restrictions on the amplitudes and the mean deformations employed. These restrictions doubtless are the result, partially at least, of the fact that chosen types of deformation have been compression, shear, and flexure, very little work having been done in cycles of elongation except at audio and higher frequencies.

[1] *Manuscript received September 26, 1949.*
Contribution No. 92 from the General Laboratories of the United States Rubber Company, Passaic, N.J.

In order to study hysteresis at high deformations and at fairly high amplitudes, an apparatus, called a spider hysterometer, has been developed for measuring hysteresis in cycles of elongation at frequencies from 2 to 60 c.p.s., at temperatures from 0° to 105°C., and over a wide range of mean elongation and amplitude. With this apparatus a comprehensive survey has been made of the hysteresis of gum stocks of Hevea and of five commercial synthetic elastomers.

Basic Principles of the Test

The principle of the spider hysterometer is not new, having been disclosed in a patent by J. W. Shields (10) in 1922; but, to the knowledge of the present authors, no data obtained in the Shields hysterometer have ever been published.

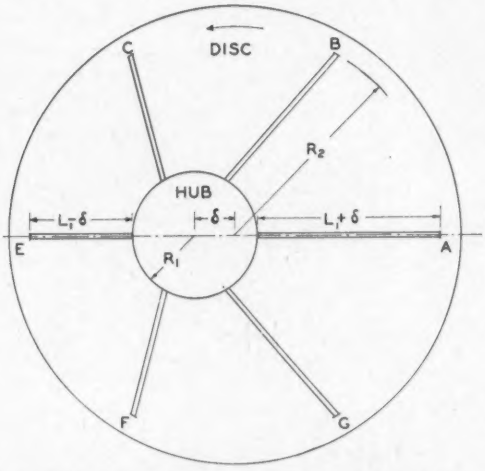

FIG. 1. *Basic design of the spider hysterometer. The large disk is driven. The small disk, or hub, rotates freely on its axis, which is forcibly displaced from the axis of the large disk. Each sample, interconnected between the two disks, executes an elongation cycle of amplitude* δ *with each revolution of the disk.*

Fig. 1 shows the essential parts of the mechanism of the spider hysterometer. Either square shouldered dumbbell samples or loop samples are attached at A, B, C, etc., on the face of a disk which can be rotated by an external motor. The axis of the disk is horizontal. The other ends of the samples are attached to a freely rotating hub mounted independently of the disk. The hub can be displaced horizontally either parallel to or perpendicular to the disk. It is seen that if the hub is displaced a distance δ parallel to the disk, the samples undergo a cyclic elongation and contraction from the values $L_1+\delta$ at position A, to $L_1-\delta$ at position E, where L_1 is the mean length of the sample in the cycle.

If the samples were perfectly elastic, the horizontal displacement of the hub would not produce any vertical reaction; but it is easily seen that any hysteresis

in the samples will produce a resultant vertical force. This follows because, with directions of rotation and displacement indicated in Fig. 1, samples above the center line are undergoing contraction, while those below the center line are undergoing extension. Because of hysteresis, therefore, a sample in position *C*, for example, exerts less tension than when in position *F*. The net vertical force on the hub is a measure of the energy loss per cycle in the six samples due to their hysteresis.

In addition to hysteresis, the mean tension is of interest and also its local variation with extension, or the dynamic differential modulus. The mean tension can be measured by the force required to produce a given displacement of the hub normal to the plane of the disk. The differential modulus is measured by the force required to produce a displacement parallel to the face of the disk; but in calculating the modulus an appreciable correction must be made for mean tension. This correction takes account of the angular asymmetry between such corresponding sample positions as *B* and *C*, for example.

Machine Construction

The construction of the machine is as shown in Fig. 2 and in the photograph, Fig. 3. The bearings and drive for the disk are of standard design and are not shown. The main mechanical feature of the hysterometer is the carriage, *ACEBH*, which supports the hub. The carriage is hung in the half-bearings *F* and *G*, in which it is free to slide horizontally as well as rotate. The bearings are lap-fitted, and are lubricated with air, fed continuously under 60 lb. pressure through a pair of small holes in each bearing.

It is seen that the hub is mounted on a lever, pivoted at point *C*, which transmits the vertical, or hysteresis, force to the Y balance beam, which rests by a knife edge on the carriage. Changes in the vertical force are balanced by shifting the rider *m* a distance *y* to the right or left. The weights on the ends

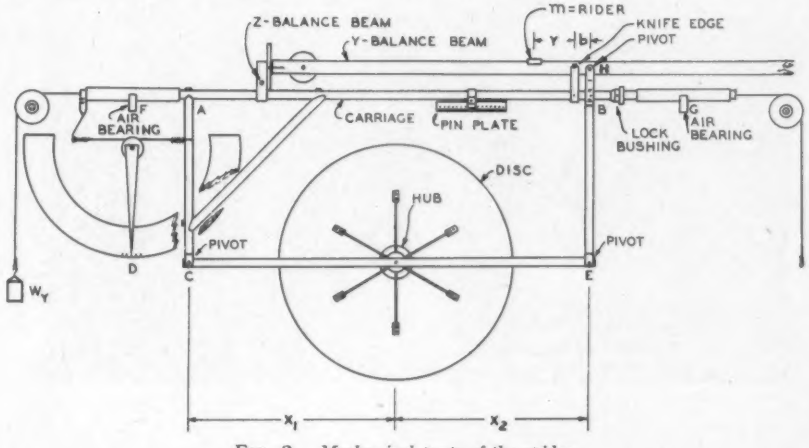

FIG. 2. *Mechanical parts of the spider.*

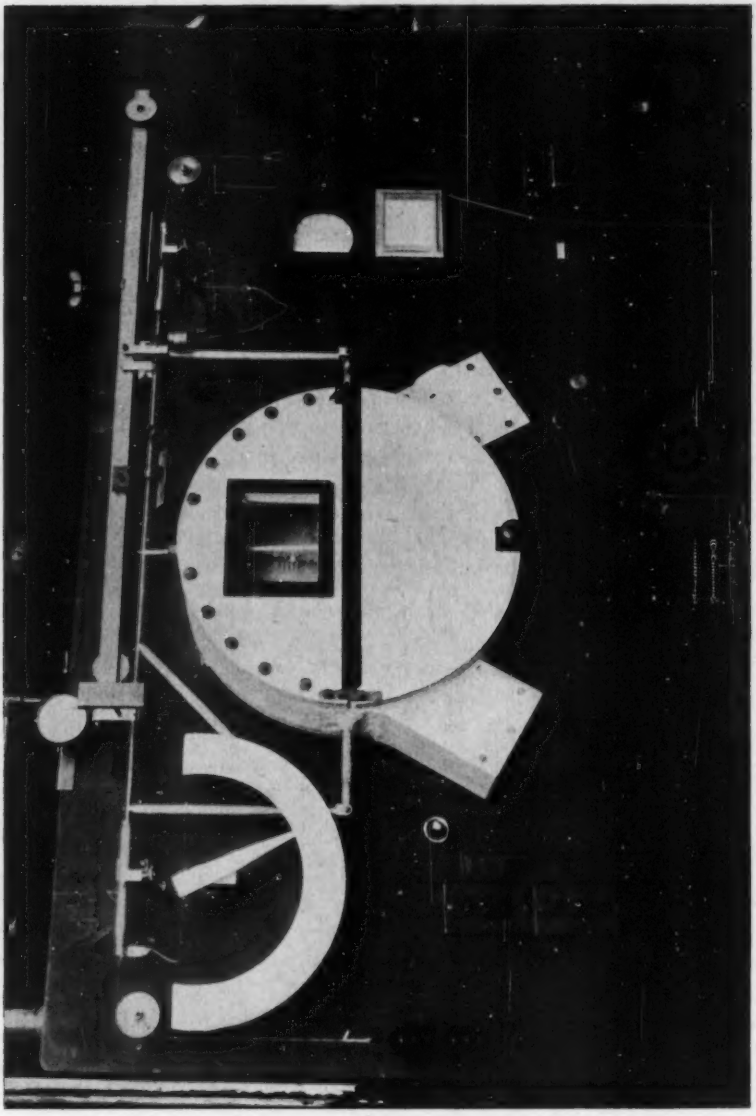

FIG. 3. *Spider hysterometer.*

of the Y beam are to increase its moment of inertia, in order to reduce the oscillations of the beam resulting from slight unbalance in the samples. The natural frequency of this beam limits the lowest speed of the disk at which measurements can be made.

To measure the radial force on the hub when displaced parallel to the disk, a weight W_y can be hung from a cord attached to one end or the other of the carriage, and the deflection of the carriage noted on the scale at D. The air bearings are important in reducing the frictional error in this measurement.

The mean tension in the samples is measured by displacing the disk along its axis a distance of approximately 1/2 in. and determining the moment acting on the Z balance beam which will retain the hub in its original position, as determined by a dial gauge in contact with the Z balance beam. This measurement is made with the disk turning and the hub radially displaced. To reduce play at the pivots, the vertical member of the vertical force-measuring linkage, EH, is locked to the carriage by means of a bushing and tapered pin at point B.

The frequency of oscillation of the samples can be fixed by adjusting the speed control mechanism which drives the disk. The speed is measured by means of a tachometer made from an automobile speedometer. The restoring spring was replaced by a weight and cam which gave a logarithmic speed scale.

The disk is surrounded by an oven, thermostatically controlled. The lever to which the hub is attached is the only part of the measuring mechanism which extends into the oven. It passes through holes with small but adequate clearance.

The range of the machine with respect to the control of the variables is as follows:

Mean extension—adjustable from 1 1/2 in. to 5 1/4 in. by means of slotted disk construction which permits attachment of the sample hooks at various predetermined positions.

Oscillation amplitude—adjustable from 0 to 2 in. in 1/4 in. steps by means of the pin-plate, or in smaller steps by means of shims. Alternatively, the amplitude can be controlled by the use of a weight W_y.

Frequency of oscillation—adjustable from 2 to 60 c.p.s.

Temperature—adjustable from 0° to 105°C. Temperatures below room temperature are obtained by forced circulation of air between the disk housing and a dry-ice cooling chamber.

Errors due to friction and windage are directional; and in order to eliminate these directional errors it was found necessary to make measurements in each case with all four combinations of positive and negative rotation and positive and negative displacement δ.

Theory

All quantities measured in this test are time averages over the period of a cycle, or the time for one revolution of the disk. In the equations involved in the analysis, terms in the second and higher powers of δ/L_1 have been neglected. To this approximation the cycle of elongation is sinusoidal.

Absolute Hysteresis

The vertical force on the hub due to hysteresis constitutes, in effect, a brake opposing the rotation of the disk. The work, W, per revolution per sample against this brake is obviously

$$W = 2\pi\delta F_y/n, \tag{1}$$

where F_y is the vertical force on the hub, δ is the horizontal hub displacement, and n is the number of samples.

This work is also the total hysteresis loss per cycle per sample. Assuming that the loss is proportional to V, the volume of the sample, and at least roughly proportional to a^2, the square of the amplitude, we define a hysteresis coefficent, H, by the equation

$$W = HVa^2. \tag{2}$$

The amplitude is defined in terms of the free length of the sample, L_0. Thus

$$a = \delta/L_0. \tag{3}$$

In terms of the measurable quantities in the test

$$\left.\begin{aligned} F_y &= Cmgy, \\ C &= \frac{x_1 + x_2}{bx_1}, \end{aligned}\right\} \tag{4}$$

where m is the mass of the rider, g the acceleration of gravity, and y is the displacement of the rider necessary to keep the Y-beam balanced when the disk is rotated. The apparatus dimensions involved in the constant C are indicated in Fig. 2.

From Equations (1) to (4) we obtain

$$H = \frac{2\pi CL_0mgy}{nA_0\delta}, \tag{5}$$

where A_0, the unstrained cross-sectional area of a sample, has been substituted for V/L_0.

The definition of y, as given, is conceptual rather than operational. As was indicated earlier, the operational definition is

$$y = \frac{(y_3 + y_4) - (y_1 + y_2)}{4}, \tag{6}$$

where y_3 and y_4 are the two high readings of the balancing rider position, and y_1 and y_2 are the two low readings, the four readings being taken with the four combinations of positive and negative disk rotation and hub displacement.

Mean Tension

The mean tension in the samples is measured by displacing the disk axially by a distance z and observing F_z, the axial force on the hub required to hold the hub in its position. Then

$$F_z = zA_0 \sum_1^6 \frac{T_i}{L_i}, \tag{7}$$

or with sufficient approximation

$$F_z = nA_0 zT_1/L_1. \tag{8}$$

Here T_i and L_i are respectively the tensile force per unit unstrained area and the length of sample i. We may take T_1 as the tensile force at the mean length $L_1 = R_2 - R_1$, where R_2 is the disk radius at the outer ends of the samples, and R_1 is the hub radius at the inner ends of the samples.

Differential Modulus

The analysis of the dynamic differential modulus and the associated radial force is somewhat involved. Referring to Fig. 4, we see readily that the mean

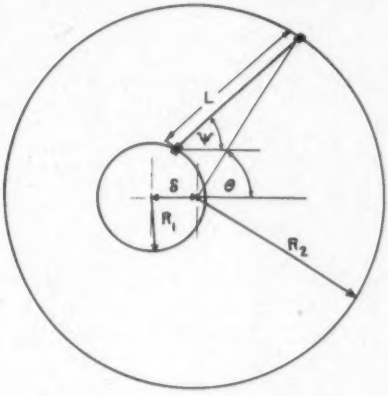

FIG. 4. *Angular and displacement relations. Geometric analysis shows that approximately*

$$\psi = \theta - \frac{\delta}{R_2 - R_1} \sin \theta.$$
$$L = R_2 - R_1 + \delta \cos \theta.$$

horizontal radial force is

$$F_r = \frac{nA_0}{2\pi} \int_0^{2\pi} T \cos \psi d\theta. \tag{9}$$

Both ψ and T, the sample tension per unit area, are functions of θ. T will be adequately represented by an expression of the form

$$T = T_1 + \frac{\Delta L}{L_0}(D + h \sin \theta), \tag{10}$$

where ΔL is the increment in length above L_1, D is the mean differential elongation modulus, and h is a constant which is proportional to H. We need not determine the proportionality factor, since h will later vanish from our equations.

It is obvious that ψ will differ from θ by only a small amount, and we may let

$$\psi = \theta + \epsilon, \tag{11}$$

and treat ϵ as a small quantity whose higher powers can be neglected. Geometrical considerations then show that, to a first approximation,

$$\left.\begin{aligned} \epsilon &= -\delta \sin \theta / L_1, \\ \Delta L &= \delta \cos \theta. \end{aligned}\right\} \tag{12}$$

The integral of Equation (9) can now be evaluated, leading to the result

$$F_r = \frac{n\delta A_0}{2L_1}\left(T_1 + D\frac{L_1}{L_0}\right). \tag{13}$$

From Equations (8) and (13) we easily obtain

$$\left.\begin{aligned} T_1 &= \frac{L_1 F_z}{nzA_0}, \\ D &= \frac{L_0}{nA_0}\left(\frac{2F_r}{\delta} - \frac{F_z}{z}\right). \end{aligned}\right\} \tag{14}$$

In these equations the tension and modulus are expressed in terms of observable quantities.

It may deserve mention that it can be shown theoretically that the hub leads the disk by a small angle which is proportional to δ and to the vertical, or hysteretic, force on the hub. The effects of this angular lead on the quantities of present interest are negligible.

Relative Hysteresis

It will be seen, in the experimental curves presented later, that hysteresis varies with mean elongation in the same general way as does the slope of a load–elongation curve. This fact suggests that, if we wish to have a measure of hysteresis which is less dependent on the elongation during the measurement, we should use the ratio of the absolute hysteresis to the differential Young's modulus. We now define the relative hysteresis R by the equation

$$R = \frac{2H}{D}. \tag{15}$$

If a weight is suspended by a rubber cord and is allowed to oscillate in a vertical line about its equilibrium height, then R, by this definition, is the ratio of the energy loss per cycle to the kinetic energy of the weight as it passes through its equilibrium position. $R/2$ is the logarithmic decrement of the oscillation.

Relations with other Hysteresis Units

The coefficient of hysteresis employed in this paper was so chosen as to be as nearly as possible independent of frequency and amplitude. It is different from the coefficients or units employed by other workers in this field, the most commonly employed unit having the dimensions of viscosity. For purposes of comparisons the following relationships will be found useful:

$$H = \pi p \eta \tag{16}$$

where $p = 2\pi\nu$, ν is the frequency, and η is the effective "viscosity" of the material at frequency ν.

$$R = 2\pi \tan \lambda = 2\Delta, \tag{17}$$

where λ is the loss angle and Δ is the logarithmic decrement.

The analysis of hysteresis in terms of these more conventional parameters is summarized in a recent review by Dillon and Gehman (1, 2).

Experimental Results

The compounds used in these tests are given in Table I, together with some of their physical properties.

The definition of hysteresis coefficient H in Equation (2) requires, if H is constant, that the energy loss per cycle shall be proportional to the square of the amplitude. A logical first experimental step is to test this relationship. Fig. 5 shows H as a function of the amplitude, a, for a GR-I gum stock at 450% mean elongation, 31 c.p.s., room temperature. It is seen that H is not constant; and the curve shows that the loss per cycle increases more slowly than a^2 up to about $a = 30\%$, after which the assumed law is approximately obeyed.

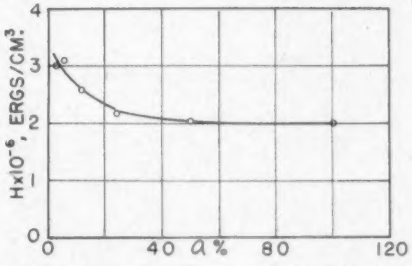

FIG. 5. *Hysteresis as a function of amplitude, a. GR-I gum stock, room temperature, 450% e, 31 c.p.s.*

TABLE I

COMPOUNDS

	Hevea	GR–S	Hycar	GR–I	Perbunan	Neoprene
Pale crepe	100					
GR–S		100				
Hycar OR–15			100			
Butyl GR–I				100		
Perbunan					100	
Neoprene GN						100
Zinc oxide	5	5	5	5	5	1
Stearic acid	2	1.5	1	3	1.5	0.5
Zinc stearate				1		
Acetone–diphenylamine condensate	1	2				
Phenyl–beta–naphthylamine			1	0.5		2
Extra light calcined magnesia						4
Piperidine pentamethylene dithiocarbamate						0.5
2-Mercaptobenzothiazole	1	1.5				
Benzothiazyl disulphide			1		1	
Tetramethyl thiuram disulphide				1		
Sulphur	2.5	1.5	1	0.5	1.2	
Cure, min	35	30	30	30	15	15
At pounds steam	30	50	50	50	50	50
Scott tensile, lb./in.^{2}	4000	188	1500	2300	396	3600
Elongation at break, %	830	1350	870	1110	620	1090
T_2, second-order transition temperature, °C	−71	−58	−23	−63	−36	−42
K, torsional hysteresis	0.038	0.289	0.229	0.182	0.178	0.092

While the variation of H with a varies considerably with the stock tested and with the testing conditions, the variation shown in Fig. 5 is about as large as any that has been observed.

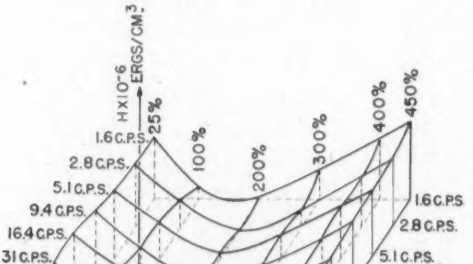

FIG. 6. *Hysteresis surface for Hevea gum stock, as a function of f, frequency, and e, mean elongation. Room temperature, 25% amplitude.*

The maximum mean elongation attainable in the spider hysterometer is limited usually by what the stock will stand without quick failure. Natural rubber is one of the few rubbers which can be tested at over 200% elongation. Fig. 6 shows the hysteresis surface for a Hevea gum stock as a function of frequency and mean elongation, at room temperature and 25% amplitude.

There is relatively little variation with frequency, which is in agreement with many other hysteresis tests (1, 2) on Hevea and other elastomers. The variation with elongation, on the other hand, is quite large. It shows a minimum at 150 to 250% elongation, depending on the frequency.

While the frequency effect is quite small, there is an interesting variation in this effect with elongation. Thus, at the lowest elongation, 25%, hysteresis increases slightly with frequency, whereas at the high elongations, 400 and 450%, hysteresis decreases slightly with frequency.

A comparison between absolute hysteresis, H, and relative hysteresis, R, is shown in Fig. 7, which includes also a curve for D, the differential modulus.

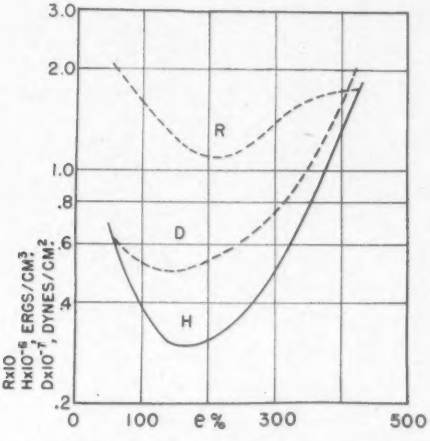

FIG. 7. *Absolute hysteresis, H, differential dynamic modulus, D, and relative hysteresis* $R = 2H/D$. *Hevea, room temperature, 11 c.p.s., 25% amplitude.*

While the D and H curves are qualitatively similar, they are far from exactly similar; and hence R is not constant, even though it shows much less variation than does H.

The results that have been reported here so far were obtained with an early model of the spider hysterometer which lacked temperature control. When the model with temperature control became available, a systematic survey was undertaken of natural rubber and the five synthetic elastomers GR-S, GR-I, Neoprene GN, Perbunan, and Hycar OR.

The samples used were all of the T-50, or square-headed dumbbell type, die cut from 1/10 in. sheets, with a shank length of 1.5 in. For each temperature a fresh group of samples was cut and installed in the machine with a minimum of stretching. The samples were not mechanically preworked. At all times precautions were taken to prevent stretching the samples beyond the elongation at which the test was to take place. As the machine works under fixed strain conditions, this was necessary to reduce as much as possible the errors that would occur in the intercomparison of various stocks which drifted by different amounts during the preworking treatment. After the samples had been installed in the jaws, the jaws were moved out along the face of the disk to the positions corresponding to the smallest mean elongation at which it was desired to work, the carriage was displaced to give the proper amplitude, and the run then made at low, then at high speed. At mean elongations other than the smallest, the samples were measured at two amplitudes, 1.5 and 25%, the smaller amplitude always being used first. Sufficient time at each test condition was allowed to permit an approach to equilibrium before measurements were made; otherwise it is impossible to balance the machine.

The net result of this testing procedure is that the samples are run on the first cycle of stretch to mean elongation, e, but on a repeated cycle of amplitude a.

Tests were made so far as possible at the following values of the independent variables:

e, mean elongation, %	16.7	50	100	200
a, amplitude, %	1.5	25		
f, frequency, c.p.s.	5	50		
T, temperature, °C.	0	35	70	105

Errors in the measurements at 1.5% amplitude are so large that these data will not be presented in detail. Other than the amplitude effects on hysteresis and modulus which are summarized in Table II, no new trend in the behavior of the samples is evident at low amplitude.

TABLE II

AMPLITUDE EFFECTS

Average ratios of 1.5% a to 25% a values
50% e, 50 c.p.s.

Stock	$\frac{H(1.5\%\ a)}{H(25\%\ a)}$	$\frac{D(1.5\%\ a)}{D(25\%\ a)}$
Hevea	1.8	1.3
GR–S	1.1	1.4
Hycar	1.5	1.1
Butyl	2.3	2.1
Perbunan	2.2	1.7
Neoprene	1.7	2.1

The following tabulation indicates broadly the response of the dependent variables to *increases* in the various independent variables:

Independent variable	*H*, Absolute hysteresis	*R*, Relative hysteresis	*D*, Differential modulus
e, Mean elongation	Decreases*	Tends to decrease	Decreases, then increases†
a, Amplitude	Decreases slightly	Decreases	Decreases
f, Frequency	Increases	Increases	Comparatively unaffected
T, Temperature	Decreases	Decreases	Decreases‡

* *H varies approximately inversely as* $1 + e$, *except for crystalline polymers, which exhibit a minimum and subsequent increase in H.*
† *Variation similar to variation of slope of static stress–strain curve.*
‡ *Except Hycar and Perbunan at low a and Hevea at low e.*

Detailed curves of *H* versus elongation at 25% amplitude, 5 c.p.s., and at various temperatures are shown in Fig. 8. It should be pointed out first that the *H*-scales are not all the same; and the hysteresis of Hevea is an order of magnitude lower than any of the others. The general trend of the curves is to decrease with elongation, but Hevea and Neoprene at the low temperatures have a minimum between 100% and 200% elongation. Temperature effects show considerable variation, both within and between stocks. The absence

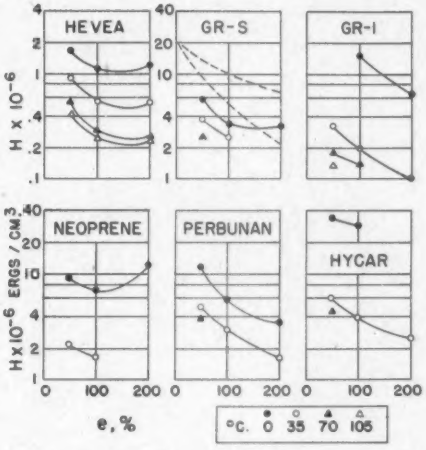

FIG. 8. *Hysteresis of all stocks, at 5 c.p.s., 25% amplitude. The dotted curves in the GR–S section, given for comparison with the experimental curves, represent the functions: upper dotted curve,* $20/(1 + e)$; *lower dotted curve,* $20/(1 + e)^2$.

TABLE III

FREQUENCY EFFECT ON HYSTERESIS, AT 35°C., 100% *e*, 25% *a*

Stock	H(50 c.p.s.)/H(5 c.p.s.)
Hevea	1.35
GR-S	1.45
GR-I	2.30
Neoprene GN	1.45
Perbunan	1.20
Hycar OR	1.45

TABLE IV

DYNAMIC DIFFERENTIAL MODULUS, $D \times 10^{-6}$, DYNES per cm.^{2}

Amplitude, 25%; frequency, 5 c.p.s.

Stock	*e*, %	*T*, °C.			
		0	35	70	105
Hevea	50	7.1	7.3	7.8	7.9
	100	5.4	5.2	6.2	
	200	6.9	5.4	5.1	5.4
GR-S	50	9.0	6.4	5.7	
	100	6.5	4.8		
	200	8.2			
GR-I	50		5.37	4.91	3.57
	100	6.36	3.33	3.93	
	200	4.50	2.17		
Neoprene GN	50	18.6	11.9(?)		
	100	21.2	13.1		
Perbunan	50	15.4	9.3	9.2	
	100	10.8	7.2		
	200	7.5			
Hycar OR	50	21.8	13.6	10.5	
	100	14.0	9.8		

TABLE V

RELATIVE HYSTERESIS AT 35°C., 50% *e*, 25% *a*, 5 c.p.s.

Stock	$H \times 10^{-6}$ ergs/cm.^{3}	$D \times 10^{-6}$ dynes/cm.^{2}	$R = \frac{2H}{D}$	4.6 K
Hevea	0.9	7.3	0.25	0.17
GR-S	3.8	6.4	1.19	1.33
GR-I	3.2	5.4	1.18	0.84
Neoprene	2.2	11.9	0.37	0.42
Perbunan	4.8	9.3	1.03	0.82
Hycar	6.0	13.6	0.88	1.03

K, torsional hysteresis, is the logarithmic decrement to the base 10 observed in a torsion pendulum of which a rubber sample constitutes the torsion member.

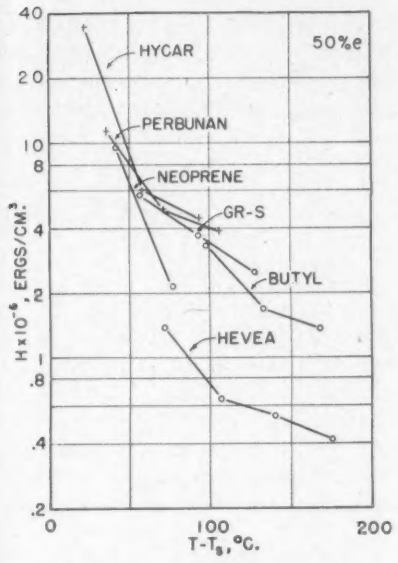

FIG. 9.

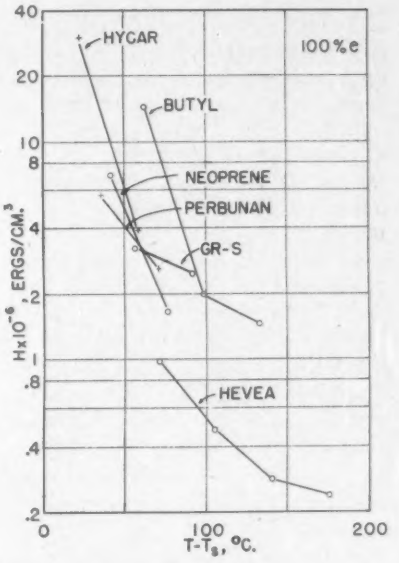

FIG. 10.

FIG. 9. *Hysteresis of all stocks, at 50% e, versus $T - T_s$, T_s being the second-order transition temperature of the respective polymer. Amplitude 25%, frequency 5 c.p.s.*

FIG. 10. *Hysteresis of all stocks, at 100% e, versus $T - T_s$, T_s being the second-order transition temperature of the respective polymer. Amplitude 25%, frequency 5 c.p.s.*

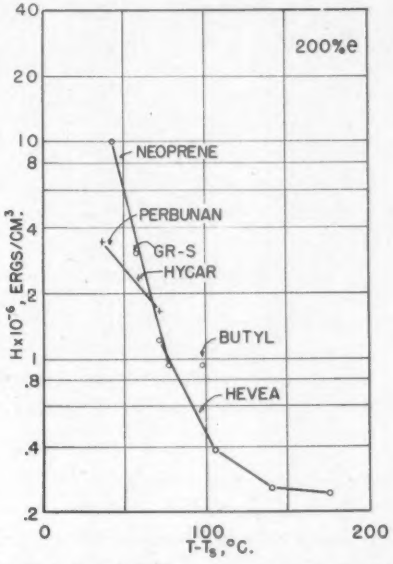

FIG. 11. *Hysteresis of all stocks, at 200% e, versus $T - T_s$, T_s being the second-order transition temperature of the respective polymer. Amplitude 25%, frequency 5 c.p.s.*

of a point for GR-I at 0°C., 50% elongation, is due to the fact that this stock is so sluggish at this testing condition that it fails to retract fast enough and buckles instead. Missing points at the higher elongations or temperatures indicate breakage of the samples under these test conditions.

The curves of H versus e for the higher frequency 50 c.p.s. are all higher but closely similar to the corresponding curves of Fig. 8. Table III shows the magnitude of the hysteresis increase with frequency as observed at 35°C., 100% e.

In Table IV are given the dynamic differential moduli observed under the test conditions covered in Fig. 8. The relative hysteresis can be computed by means of Equation (15) from the data of Fig. 8 and Table IV. In Table V, R is tabulated for 50% e, 35°C. The torsional hysteresis, K, (8) is the damping factor to the base 10. It is therefore obvious from Equation (17) that theoretically, if relative hysteresis were independent of extent and type of deformation, we should expect to find $R = 4.6\,K$. Values of K at room temperature for this comparison were taken from Table I. It is seen in Table V that the expected relationship holds approximately, but there are several definite discrepancies.

If R is calculated for 100% elongation, and this value combined with R at 50% elongation to find an extrapolated value for 0% elongation, corresponding to the elongation conditions of the torsional test, we still find discrepancies between R and $4.6\,K$.

A comparison of the hysteresis values in Fig. 8 with the T_s values in Table I suggests a correlation: the higher the T_s, the higher the hysteresis. In view of this fact, Dr. H. M. Smallwood suggested to the authors that our hysteresis data be plotted against $T-T_s$. This has been done in Figs. 9, 10 and 11. It appears that the correlation mentioned does in fact exist, that the correlation improves as elongation increases, and that at 200% elongation Hevea is quite in line, though it is definitely out of line at the lower elongations. GR-I, on the other hand, while in line at 50% elongation, is out of line at 100%. Data at 200% are lacking.

Discussion

The data that have been reported here show that hysteresis is a more complex phenomenon in several respects than has been shown by other published measurements. Some of these complexities we can understand or explain qualitatively; others defy explanation on the basis of current theories of hysteresis.

Among the unexplainable results is the variation in H with amplitude shown in Fig. 5. The present trend in theoretical work is towards a comprehensive theory of all relaxation phenomena based on an assumed assembly of relaxing units with a distribution or spectrum of relaxation times; but such a theory predicts a hysteresis loss strictly proportional to amplitude squared.

The observed increase in hysteresis at high elongations in Hevea and Neoprene shown in Figs. 6 and 8 may be attributed to crystallization effects. The experiments of Long, Singer, and Davey (7) and Holt and McPherson (6) have established that there is a time lag in the crystallization of stretched Hevea; and we may reasonably assume the same for Neoprene, which, like Hevea, is known to crystallize when stretched. Since crystallinity has a strong effect on modulus, hysteresis in crystallinity would add mechanical hysteresis to that already present due to other causes.

Since the time lag in crystallization is of the order one second, a cycle of elongation at our high frequencies will be completed before the crystallization at the high end of the cycle has time to approach its equilibrium value. Hysteresis associated with crystallization will therefore be reduced at high frequency. Thus is explained qualitatively the reversal at high elongations in the sign of the normal frequency effects.

The choice of e as an independent variable in Figs. 6 and 8 is arbitrary and perhaps not the best choice to bring out any relationships that might be expected between hysteresis and the mean elongation. For example, it might be felt that hysteresis would vary as the square of the amplitude, but with amplitude defined as δ/L_1 rather than as δ/L_0. If this were the case, we would then have $H = \dfrac{H_1}{(1+e)^2}$, where H_1 would be invariant with e. The lower dotted curve in the GR-S section of Fig. 8 is of this form. The upper dotted curve is of the form $H_1/(1+e)$.

Omitting from consideration the crystallizing elastomers Hevea and Neoprene, we see in Fig. 8 that the data for GR–S and Hycar–OR fit better the curve $H = H_1/(1+e)$, while the data for GR–I and Perbunan fit better the curve $H = H_1/(1+e)^2$. If any simple general law exists for H as a function of e, at least some of the present data are somewhat in error and fail to indicate the law.

Regarding the normal frequency effect, the data of Table V show that for a frequency ratio of 10/1 the increase in H is only by a factor of 2.3 in one extreme case, the usual factor being about 1.4. For a single relaxation mechanism of the purely viscous type, that is, one for which the relaxation time is small compared with the period of the cycle, the increase in H would be in the ratio 10/1.

By piecing together the results of the present authors and the published results of other workers, it can be shown that absolute hysteresis of rubber increases very slowly and almost linearly with log frequency over at least three decades (11). To explain this fact by a distribution of relaxation times would require an extremely broad distribution, which would be difficult to account for in terms of molecular mechanisms of the relaxation process. Perhaps the true explanation of hysteresis must be made in terms of relaxing elements which in themselves are nonlinear in their behavior. Such nonlinear

elements are postulated in some recent theoretical work on relaxation phenomena in rubbers (9) and in textiles (3, p. 61).

The assemblies of curves in Figs. 9, 10, and 11, showing rough correlations between H and $T-T_s$ for all polymers, indicate the important conclusion that hysteresis at all temperatures arises primarily from the same molecular mechanisms or interactions as those which develop brittleness when the temperature is reduced to T_s. The departures, under some test conditions, of Hevea and GR–I from the average curves are larger than the estimated experimental error. Hence, there are also other, as yet unknown, factors involved in hysteresis.

References

1. DILLON, J. H. and GEHMAN, S. D. India Rubber World, 115: 61-68; 76; 217-222. 1946.
2. DILLON, J. H. and GEHMAN, S. D. Rubber Chem. and Technol. 20: 827-858. 1947.
3. EYRING, H. and HALSEY, G. *In* High polymer physics, *edited by* H. A. ROBINSON. Remsen Press, Brooklyn, N.Y. 1948.
4. GROSS, B. J. Applied Phys. 18: 212-221. 1947.
5. GROSS, B. J. Applied Phys. 19: 257-264. 1948.
6. HOLT, W. L. and MCPHERSON, A. T. J. Research Natl. Bur. Standards, 17: 657-678. 1936.
7. LONG, J. D., SINGER, W. E., and DAVEY, W. P. Ind. Eng. Chem. 26 : 543-547. 1934.
8. MOONEY, M. and GERKE, R. H. India Rubber World, 103: 29-32. 1941.
9. MOONEY, M., WOLSTENHOLME, W. E., and VILLARS, D. S. J. Applied Phys. 15: 324-337. 1944.
10. SHIELDS, J. W. U.S. Patent 1,595,318. August 10, 1926.
11. VILLARS, D. S. Unpublished survey.